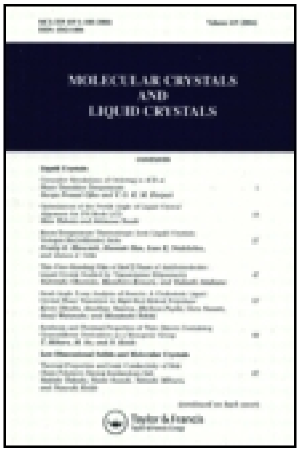

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Crystal Structure of 1-(2-Thienyl) Penta-1,3-Diyne-5-OL

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1-(2-thienyl)penta-1,3-diyne-5-ol (TD-OL), C_9H_6OS, $M_r = 162.2$, orthorhombic, Pbcn, $a = 22.660(2)$, $b = 7.482(1)$, $c = 9.379(1)$ Å, $V = 1590.0(3)$ Å^3, $Z = 8$, $D_c = 1.355$ Mgm^{-3}, $\mu = 0.338$ mm^{-1}, F(000) = 672, $\lambda(\mathrm{MoK}_\alpha) = 0.71069$ Å, final R and $wR2$ are 0.044 and 0.1266 respectively.

Keywords: Crystal structure; 1-(2-thienyl)penta-1,3-diyne-5-ol; solid state reactivity; nematic

INTRODUCTION

The synthesis of new liquid crystalline materials has gained greater momentum, both from the point of technology and academic interest due to their exotic physical properties. Mesogens with different rigid groups and varying chain lengths are being synthesized. Also, it is of great value to establish structure-property relationship. As a part of the broad study aimed at evolving structure-property correlation, we have synthesized a number of diacetylenes having heteroaryl moieties as subtituents. These monomers are aimed

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[*] Correspondence address.

for solid state polymerization wherein they transform to polydiacetylene via, 1,4-addition reaction, having highly conjugated backbone. The reaction is topochemical in nature. Not all the diacetylenes react to form the polymer, the polymerization being governed by the packing geometries of the monomer molecules in crystal. Thus when the diacetylene containing 2-thienyl group at both ends was exposed to heat, UV or gamma radiation, it did not react to form the polydiacetylene. However, the monomer showed liquid crystalline behaviour when heated [1]. To investigate further, we synthesized another diacetylene, 1-(2-thienyl)penta-1,3-diyne-5-ol which has 2-thienyl and —CH_2OH as the substituents. This compound also shows liquid crystalline behaviour. But it does not polymerize in solid state to provide the corresponding polydiacetylene. Here, we report the structure of 1-(2-thienyl)penta-1,3-diyne-5-ol.

EXPERIMENTAL

The little compound was synthesized using the reported procedure [2]. The monomer was obtained as light brown solid which was crystallized to get single crystals from acetonitrile at 35°C. Light yellow needle shaped crystals of TD-Ol were obtained after three days. The compound exhibits nematic phase in the range 85–115°C. The accurate cell dimensions and orientation matrix were obtained by a least-squares fit to the setting angles of 25 reflections on Enraf-nonius computer controlled four circle diffractometer employing MoK_α radiation. Two reflections measured every one hour showed no deterioration of the crystal. Lorentz and Polarization corrections were applied. The crystal structure was solved by SHELXS-86 [3] and was refined by full marix least-squares using SHELXL-93 [4] [1168 unique reflections with $I > 3\sigma(I)$]. The difference Fourier maps were used to locate the positions of hydrogen atoms except the one attached to oxygen atom. The O—H hydrogen was fixed at the chemically acceptable position with (C—H 0.85 Å). This was done due to the difficulty of finding the hydrogen maxima from the electron density map around the oxygen atom which was showing a certain amount of thermal disorder. All the hydrogen atoms located through difference map were least-squares refined with isotropic thermal parameters assigned to them. 125 parameters have been refined

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The observed and calculated structure factor tables can be obtained from the authors.

using 1168 unique reflections to $R = 0.044$, $WR2 = 0.1261$. In the final difference map $(\Delta\sigma)_{max} = 0.001$ and $(\Delta\rho)_{min} = -0.252$, $(\Delta\rho)_{max} = 0.290$ Å^{-3}. All calculations were performed on Micro Vax 3100 computer.

RESULTS AND DISCUSSION

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table I. Anisotropic parameters (U_{ij}) for the non-hydrogen atoms are listed in Table II. The Table III gives the bond distances and angles of non-hydrogen atoms. Figure 1 represents the ORTEP [5] diagram of the molecule with thermal ellipsoids at 50% probability.

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$) with e.s.d's in parentheses for the non-hydrogen atoms. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
S	2153(1)	900(1)	3874(1)	552(3)
C(1)	2181(1)	1843(5)	2230(3)	536(6)
C(2)	1765(2)	3101(5)	2056(3)	574(9)
C(3)	1408(1)	3381(4)	3272(3)	493(8)
C(4)	1567(1)	2235(4)	4362(3)	424(7)
C(5)	1306(1)	2106(4)	5734(3)	470(7)
C(6)	1074(1)	2035(4)	6876(3)	482(7)
C(7)	808(1)	2029(4)	8184(3)	466(7)
C(8)	572(1)	2059(4)	9330(3)	462(7)
C(9)	275(1)	2163(4)	10709(3)	484(7)
O	197(1)	3960(3)	11120(2)	556(6)

TABLE II Anisotropic displacement parameters (Å^2 $\times 10^3$) for the non-hydrogen atoms with e.s.d's in parentheses. The anisotropic displacement factor exponent takes the form: $-2\Pi^2[h^2a^{*2}U11 + \cdots + 2hka^*b^*U12]$

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
S	64(1)	61(1)	41(1)	-1(1)	8(1)	14(1)
C(1)	61(2)	63(2)	37(2)	-5(2)	8(1)	-8(2)
C(2)	61(2)	66(2)	44(2)	13(2)	-5(2)	-9(2)
C(3)	44(2)	55(2)	49(2)	6(1)	1(1)	4(1)
C(4)	43(2)	46(2)	39(1)	-8(1)	2(1)	-4(1)
C(5)	49(2)	49(2)	43(2)	-8(1)	4(1)	0(1)
C(6)	52(2)	48(2)	45(2)	-7(1)	7(2)	2(1)
C(7)	54(2)	41(2)	45(2)	-6(1)	4(1)	0(1)
C(8)	54(2)	41(2)	44(2)	-5(1)	6(1)	1(1)
C(9)	66(2)	41(2)	39(2)	0(1)	11(1)	0(1)
O	79(2)	45(1)	43(1)	-5(1)	10(1)	9(1)

TABLE III Bond lengths [Å] and angles [deg.] involving non-hydrogen atoms with e.s.d's in parentheses

S-C(1)	1.697(3)
S-C(4)	1.723(3)
C(1)-C(2)	1.342(5)
C(2)-C(3)	1.413(4)
C(3)-C(4)	1.382(4)
C(4)-C(5)	1.419(4)
C(5)-C(6)	1.195(4)
C(6)-C(7)	1.367(4)
C(7)-C(8)	1.200(4)
C(8)-C(9)	1.460(4)
C(9)-O	1.410(3)
C(1)-S-C(4)	91.7(2)
C(2)-C(1)-S	112.1(2)
C(1)-C(2)-C(3)	114.0(3)
C(4)-C(3)-C(2)	110.9(3)
C(3)-C(4)-C(5)	127.1(3)
C(3)-C(4)-S	111.3(2)
C(5)-C(4)-S	121.5(2)
C(6)-C(5)-C(4)	178.0(3)
C(5)-C(6)-C(7)	177.6(3)
C(8)-C(7)-C(6)	178.7(3)
C(7)-C(8)-C(9)	177.8(3)
O-C(9)-C(8)	110.5(2)

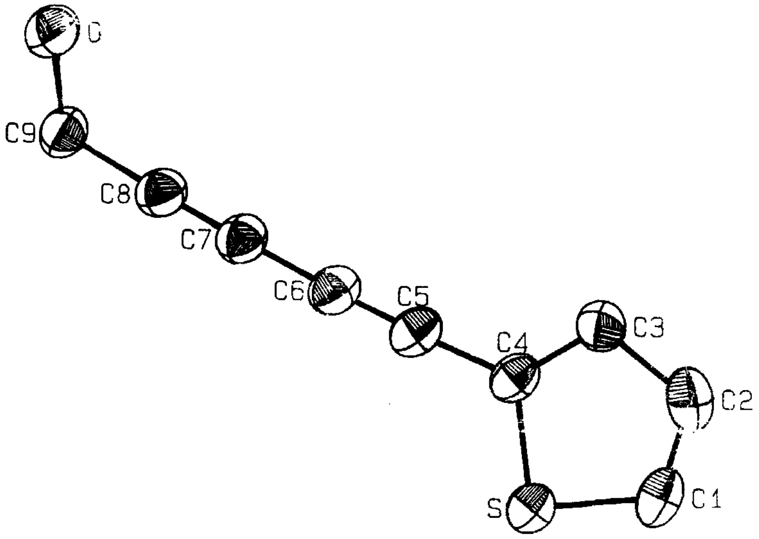

FIGURE 1 ORTEP diagram of the molecules.

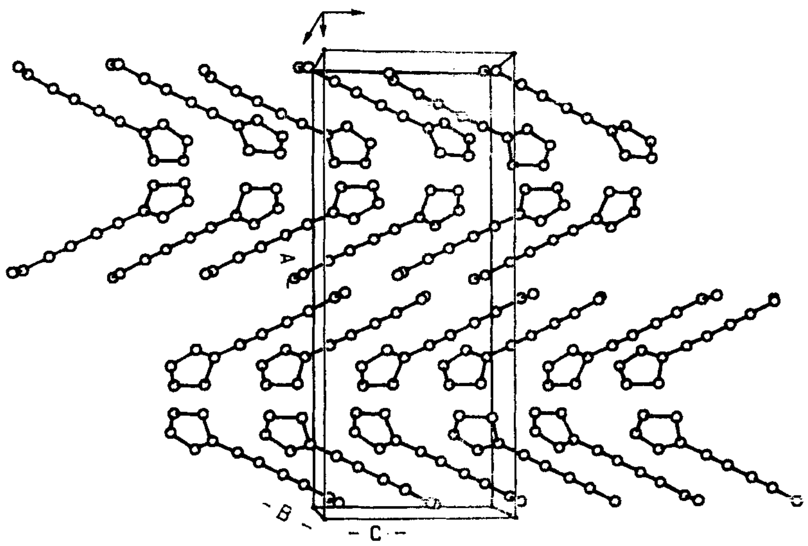

FIGURE 2 Imbricated arrangement of molecules.

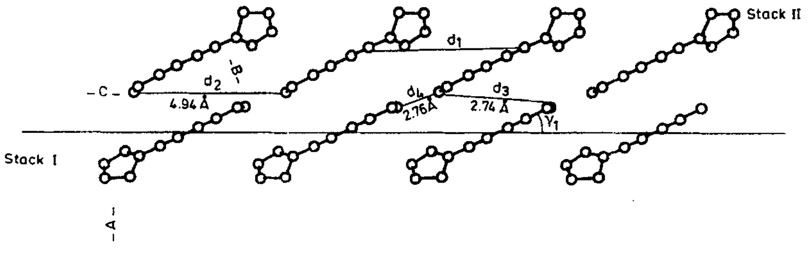

FIGURE 3 Stacking of the molecules along *c* axis.

Figure 2 shows that the molecules of alternate stacks are imbricated. Figure 3 shows stacking of the molecule along *c* axis.

The molecules are stacked along the crystallographic *c* axis (Fig. 3). The sulphur is positioned in the five membered ring. The torsion angle [C(5), C(4), S, C(1) is 179.8(3)° and C(5), C(4), C(3), C(2) is − 179.1(3)°]. This indicates that the five membered ring [S, C(1), C(2), C(3), C(4)] is in a plane with C(5) atom. The chain C(4), C(5), C(6), C(7), C(8), C(9) is almost linear as expected. The molecules in the packing diagram are related through a centre of inversion about the body centre.

The single crystal structure analysis of TD-O1 also reveals that packing arrangement is not ideal for this diacetylene for making it reactive in solid state. The distance between two adjacent diacetylene units is d_1[C(5)-

C(5′)] = 5.643 Å. The angle between the diacetylene unit and the stacking axis i.e *c*-axis is $\gamma_1 = 51.54^\circ$ and $S_1 = d_1 \sin(\gamma_1) = 4.42$ Å (Fig. 3). Thus, the values for two of the above parameters are far away from the ideal values for solid state polymerization to occur [6–8]. Experimentally also, it is found that this diacetylene is unreactive in solid state.

The molecule and its equivalent (x, $-y$, $1/2 + z$) form approximate stacks as represented in I or II in Figure 3. The distance (d_2) between the oxygen of consecutive molecules in the stack is 4.94 Å and this may not lead to strong packing force. However, oxygen's of adjacent antiparallel stack II are at distances of 2.74 Å(d_3) and 2.76 Å(d_4) from the corresponding oxygen's of stack-I. This results in strong dipolar interaction between two adjacent stacks and is responsible for holding the individual stacks together. Pairs of antiparallel stacks form a very strong imbricated chain of molecules in the *c*-axis direction which should be responsible for the substance to be a nematogen.

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